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Preparation/Characterization of Plasticized Poly (Lactic Acid) For Packaging Applications

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Abstract

In this research an attempt is made to modify the brittle poly (Lactic acid) (PLA) into flexible PLA by adding Poly (Butylene Succinate) (PBS), Poly (Ethylene Glycol) (PEG) and Ricinoleic acid (R.ACID) as a plasticizer. Various plasticizers with different weight % of plasticizers - 10%, 20% and 30% in wt% for PLA/PBS, 5, 10 and 15% for PLA/PEG and PLA/R.ACID are used to make sheets. With the addition of plasticizers, the failure mode changes from brittle fracture of neat PLA to ductile fracture of the plasticized PLA, upon plasticization glass transition temperature (Tg) decreased from 62°C to 46ºC. With the increase of plasticizers content, the tensile strength and modulus of the PLA decreased slightly while the elongation at break and toughness of plasticized PLA were increased (from 5.7 to 11.9%). Further tear strength increased to maximum value of 36 MPa. SEM analysis confirms that plasticizers were uniformly distributed in PLA matrix**.**

Key words: Poly (Lactic acid); Poly (Butylene Succinate) (PBS); Poly (Ethylene Glycol) (PEG); Ricinoleic acid (R.ACID); plasticizers

1. Introduction

Currently, petroleum based polymers such as Poly (propylene), Poly (ethylene) etc. are being widely used in packing industries for packing food/snacks applications. Due to the littering habit of society, it remains in the street since these are not bio degradable/compostable thus affect the environment. Therefore replacement of petrochemical based polymers with biodegradable polymers can give a solution for plastic waste management. PLA is a potential candidate for suitable replacement of petrochemical polymers because it is biodegradable with reasonable mechanical properties and heat resistance however due to brittleness nature and high crystallinity 35-40% results PLA has a limitation in processing of packing industries.

The flexibility of PLA can be improved by modifying its physical properties and mechanical by blending PLA with a plasticizer or a second polymer. A large number of investigations have been performed on the blending of PLA with various polymers. For example Poly(butylene adipate) (PBA) [1], phenolic antioxidants [2] Poly(1,3-butanediol), Dibutyl sebacate, Acetyl glycerol monolaurate, Poly(ethyleneglycol) [3], ethylene-co-vinyl acetate (EVA) [4], poly(butylene adipate-co-terephthalate) (PBAT) [5], α-tocopherol, BHT [6], Tributyl citrate oligomers (TBC) [7], and poly(D,L-lactide)-b-poly(ethylene glycol) copolymers [8]. Blending PLA with various polymers is one of the most popular choices in order to improve its properties, and at the same time to bring down the product cost. The blends included poly (3-caprolactone) (PCL), poly (ethylene-co-vinyl alcohol) (EVOH) [9], polyolefin, and starch [10]. Peng Zhao et al.,[11] reported that, biodegradable polyesters, that is, poly(butylene adipate) (PBA), poly(butylene succinate) (PBS), and poly(butylene adipate butylene terephthalate) (PBAT), were blended with PLA. Blends show considerably higher elongation at break than pure PLA with an acceptable loss of strength. The elongation at break increases at the higher polyester contents with the maximum value (>600%) occurring at a PBAT content of 15%. Addition of PBAT into PLA may improve the toughness of PLA. Moreover, the crystallizability of PLA component of blends can be increased by the addition of a small amount

of PBAT. Blending PLA with the oligomeric plasticizers lowered the glass transition temperature. The plasticization effect was larger with low molecular weight plasticizers [7]. In a work done by V. P. Martino et .al, [12] four plasticizers(Di-2Etylhexyl Adipate (DOA), and three commercial polymeric adipates (polyesters of adipic acid) with different viscosities, named as G206/3, G 206/5 and G 206/7) blended with PLA and found that elastic modulus was seen to decrease as the concentration of plasticizers increased. Results indicated that the flexibility of the tested films had increased, and considering this mechanical property the most important for packaging, we think it is a potential application of plasticized PLA films. Resistance to tear propagation is another important property for these applications, and has also shown improvements. Many literature studies has been used plasticizer with polymer blend to improving the mechanical properties [12-19]

The objectives of the present study were to prepare and characterization of plasticized PLA and thereby obtaining sheet of increased flexibility for potential use in packaging material applications. Different plasticizers like Poly (Butylene Succinate) (PBS), Poly (Ethylene Glycol) (PEG) and Ricinoleic acid (R.ACID) used at different proportions. It is demonstrated that R.ACID increased the ductility of PLA more efficiently than other plasticizers (PBS and PEG).

2. Materials and methodology

Commercially available PLA (Poly MBQ 3D), poly (butylene succinate) (PBS) [glass-transition temperature (Tg) = 62°C and melting temperature (Tm) =155°C], Poly (Ethylene glycol) (PEG) 4000 (Tm= 60ºC) and Ricinoleic acid (R.ACID) were obtained from Local suppliers. (Chennai, India). Pre-heating was done with 180ºC for PLA, 60ºC for PBS, 30ºC PEG for 12 hours before blended with plasticizers. PLA and plasticizers were blended and extruded as sheet in HAAKE RHEOCORD 9000 FUSION with screw rotation sped of 150 RPM, screw torque 45-50 Nm, and zone temperature of 120, 130, 150 and 160 °C .

2.1. Characteristics

DSC was carried out using a TA instrument, DSC Q20. Each sample was scanned to a temperature of 200 ºCat a rate of 10 ºC and cooled under the rate of 50 ml/min. the thermal properties, melting temperature (Tm), glass transition temperature (Tg) and crystallization temperature (Tc) were determined from the scan after the material was quenched-cooled from molten state. Melting temperature was considered the maximum of the endothermic melting peak. Crystallization temperature was observed as the exothermic peak was taken as Tm. Weight of the sample was 8-10 mg.

Thermogravimetric analysis (TGA) was carried out using a TA instrument, DSC Q20. Each sample was scanned to a temperature of 600 ºC at a rate of 10 ºC with a flow of nitrogen atmosphere rate of 40 ml/min.The tensile strength was performed as per ASTM D882 for tensile test on Instron Bluehhill. The blended sheets are were cut into rectangle shape (50 mm x 250 mm). The machine was operated at cross-head speed of 5 mm/min. The tear strength was performed as per ASTM D624 for tear test on Instron Bluehhill. The blended sheets are were cut according to the standard tear resistance measures the ultimate force required to tear sheet. The MFI of the PLA and plasticized PLA was determined according to ASTM D 1238 at 190°C under load of 2.16 kg using Melt Flow Index testing equipment (LLOYD Instruments, London). The apparent density of films was measured using a SARTORIOUS analytical balance (Model ME 215S) equipped with density measurement accessory (Model YDKOA). Water was used as the liquid medium. Surface of the materials were studied with ZEISS scanning electron microscope (SEM) with an accelerating voltage of 10 KV. The sample were coated with gold to avoid charging under the electron beam.

3. Result and discussion

3.1. Tensile strength

The main goal of plasticizer addition into PLA matrix was to decrease its rigidity and increase ductility of PLA. It is worth noting that neat PLA at room temperature was characterized

by low elongation (nominal strain at break = 5.7%) together with high tensile strength (45 MPa). The most important modifications of tensile properties by plasticization have been observed at relatively high percentage of plasticizer (10-20%), these effects are discussed.

Amorphous PLA exhibits the Tg in the range of 62 ºC. At this temperature, PLA shows high tensile strength and is quite brittle. Adding plasticizer to PLA enhanced plastic elongation and reduced brittleness. The addition of a plasticizer caused a decrease in the Tg of PLA. It is recognized that the mechanical properties of polymers depend on the test temperature with respect to Tg. When Tg of the polymer approaches the test temperature, a significant decrease of the tensile strength (TS) and an increase of the elongation at break (%E) of PLA sheet have been reported [13].

Pure PLA fails as soon as it passes the yield stress. Apparently, pure PLA has a strong strain softening which, however, is not stabilized by a strain hardening. Upon drawing, strain softening stimulates strain localization which causes the build-up of local tri-axial stresses. If the local strain could not be delocalized, this local tri-axial stresses will induce void nucleation and crazes in the matrix leading to brittle failure behaviour. For this reason, PLA is brittle. It can be found that the fracture behaviour of the specimens in the tensile tests changes from brittleness of neat PLA to ductile fracture of binary blends. The binary blends show an initial strain softening after yielding and then undergo considerable cold drawing. The stress–strain curve after the yield point shows a combination of strain softening and cold drawing. In this region, there is competition between the orientation of PLA chains and crack formation. Hence, there is a drop in stress with increasing strain. The elongation at break of PLA blends was improved dramatically with the increase of plasticizer content.

Table 1. Tensile strength, Modulus, Elongation at break and Tear strength for neat PLAand plasticized PLA

Materials	Tensile strength (mpa)	Modulus (mpa)	Elongation at break (%)	Tear strength (mpa)
PLA 100%	45.3	1205.70	5.7	19.5
PLA90%PBS10%	44.9	1193.2	5.9	23.9
PLA80%+PBS20%	44	1190.9	6	26.9
PLA70%+PBS30%	43.5	1178.6	6.3	30.8
PLA95%+PEG5%	38.4	1048.9	7.6	24.2
PLA90%+PEG10%	34	1021.9	6.2	29.8
PLA85%+PEG15%	29.3	1016.1	9.4	33.3
PLA95%+R.ACID5%	40.7	1021.9	6.9	21.5
PLA90%+R.ACID10%	31.4	848.1	8.3	28.1
PLA85%+R.ACID15%	27.4	697.6	11.9	36.1

As summarized in Table 1, addition of plasticizer had lead to an expected decrease of tensile strength explained by lower macromolecular chain cohesion. The PLA has a maximum tensile strength of 45 MPa, while the plasticized compositions were found to have reduced tensile strength, and generally, this decrease (from 4.5 MPa to 27.4 MPa) is quite well correlated with the percentage of plasticizer(5,10 and 15%). The comparison of the plasticized compounds PLA/PBS, PLA/PEG and PLA/R.ACID confirms again an excellent plasticizing effect induced by the addition of plasticizers. Correspondingly the modulus were found to decreased from 1205 MPa (for neat PLA) to 697 MPa (for PLA/ R.ACID 5%)

A pronounced elongation at break was observed for all the PLA/R.ACID blends the tensile strength started decreasing with the increase of R.ACID content from approximately 40 MPa to 27 MPa. PLA/PEG blends also showed decrease in tensile strength with the corresponding increase in PEG content in PLA matrix approximately from 38 MPa to 29 MPa. But the behaviour of PLA/PBS blends are contradiction with results obtained from other plasticized PLA. Tensile strength seems to be retained with in an interval of 1 MPa.

The elongation at break of the blends increases from 5.7% for neat PLA. Addition of PEG with different concentration showed variation of elongation at break from 7.6% to 9.4%. R.ACID shows steep increase in elongation at break from 6.11 % to 11.9 % with increase in R.ACID content. Since tensile strength is retained in the PLA/PBS blend, elongation at break shows no significant change: starts from 5.9 % to 6.3% only. Since, maximum elongation at break of 11.9% is obtained by blending 15 wt% of R.ACID it can be infered that R.ACID is an excellent plasticizer for PLA.

3.2. Tear strength

Tear strength is the force it takes to rip a plastic film. Generally plastic sheet with a property of brittleness will have very low tear strength; this is clearly proved from the Table 1. Since neat PLA is a brittle material it shows maximum stress around 19.5 MPa only. It is obvious that addition of plasticizers disturbs the strong force of bonding between the molecules by embedding themselves between the chains of polymers, spacing them apart, thereby increasing the free volume and ultimately increasing the tear strength of the blends. As the percentage of plasticizers increases in the blend tear strength seems to increase with a regular correlation between percentages of plasticizer and tear strength.

The maximum stress observed is 36.1 MPa, which is about 185% higher than that of neat PLA (19.5 MPa) for R.ACID 15%. When PBS is used in PLA for plasticizing effect, it was noted that maximum stress is 30.86% with 30% content in PLA. Whereas in R.ACID, it is found to be 33.3 MPa for 15% content. Tear strength was found to increase with increase in plasticizer content in PLA matrix, change in maximum stress is perfectly correlated with percentage of plasticizer content.

3.3. Thermal analysis

Since the glass transition temperature (Tg) is an excellent indicator of chain mobility, plasticizing efficiency has therefore been evaluated by measuring the decrease of Tg as a function of plasticizer concentration. All the blends realized in this work show only one Tg in the DSC diagrams indicating a good miscibility between polymer and plasticizer. The decrease of Tg highlights the effect of the plasticizer in PLA compositions with increasing molecular mobility. The plasticizing effect is confirmed by the modification of Tg which is significantly decreased by comparison with the neat PLA matrix. On the other hand, by considering the PLA-PBS/PEG/R.ACID blends it should be noted that the decrease of Tg is quite well correlated with the plasticizer content, whereas in a similar correlation Tm slowly decreased with the amount of plasticizer. Multiple endothermic peaks were found because of additional cold crystallization processes, the peak temperature of the largest endotherm was taken as the melting temperature.

Finally, from DSC measurements it comes out that addition of 15 wt% of PEG and R.ACID blends into PLA can lead to a significant decrease of Tg with respect to the neat polyester matrix and therefore improved ductility toughness can be expected. Exemplary heating thermograms of the sheet of neat PLA and plasticized PLA are shown in Tg of blends was always lower than that of neat PLA. The plasticizer decreased Tg from about 62.2ºC (for neat) PLA to 46.5 ºC for the blends with different proposition of plasticizers. The lower values of temperature ranges correspond to the glass transition temperatures of PLA blended with R.ACID and PEG (at different wt%), while the higher to those of PLA blended with PBS (at different wt%). The Tg values were lower than those of measured virgin PLA by DSC at the same heating rate, especially in the case of R.ACID, and also the melting temperature of PLA/R.ACID 15% was lower than that of pure PLA.

In terms of efficiency, it has been observed that blends containing 30% of plasticizer (R.ACID) exhibit the lowest value of 46.5ºC. PEG as a plasticizer reduces the Tg upto 50.1ºC. Using PBS as a plasticizer does not show any significant change in Tg (as same as virgin PLA). The effect of plasticizers PBS, PEG and R.ACID on PLA are different, while PBS was less efficient with respect to PEG and R.ACID.

The use of plasticizers reduced the crystallization temperature by 105-106ºC from

the value of 113.4ºC found for neat PLA film. All the plasticizers somehow hinder polymer chain lateral rearrangement and hence crystallize the PLA. For neat PLA, a broad crystallization peak was observed between 95ºC to 105ºC. It was followed by a sharp melting peak at around 154ºC. A direct proof of polymer miscibility can be obtained by observing the change in Tg and Tm of the polymer blends.

Table 2. Tg, Tc, Tm and Td values of neat PLA and plasticized PLA

Materials	Tg(ºC)	Tc(ºC)	Tm(ºC)	DECOMPOSITION TEMP.Td (ºC)
PLA 100%	62.2	113.4	155.7	360
PLA90/PBS10%	61.6	107.7	154.9	360.2
PLA80%/PBS20%	62.3	106.2	154.1	361.4
PLA70%/PBS30%	62.7	99.5	153.7	363.8
PLA95%/PEG5%	60.5	116.2	155.4	365.8
PLA90%/PEG10%	56.9	106.6	154.5	366.3
PLA85%/PEG15%	50	90.4	154.2	370.5
PLA95%/R.ACID5%	52	110.9	154.7	359
PLA90%/R.ACID10%	47.7	108.6	151.6	355.3
PLA85%/R.ACID15%	46.5	105.8	151.2	348.9

Melting of PLA began above 90 ºC in all the materials. Single melting peak, centred at 150 ºC was observed for neat PLA. In the blends, with the increase of the plasticizer content the melting peak shifted gradually to a lower temperature, at most to 151.2ºC for PLA/PEG 15% and for PLA/R.ACID 15% is 151.5ºC.

For the entire composition range investigated, two distinct melting peaks were also observed, indicating that each component crystallized individually. Two peaks were attributed to re-melting of newly formed crystallite during heating. Lee S and Lee J.W [14] stated that appearance of double endothermic peaks due to quenching after the first heating cycle. It does not give sufficient time for high melting crystallite to form. Therefore, more low crystallites were formed. An issue not very often taken into account when studying a plasticized polymer is the impact of the plasticizer on the thermal stability of the polymeric matrix. To investigate the influence of the presence of plasticizers on the thermal stability of PLA matrix, TGA measurements were carried out on the different formulations. From TGA thermogram the decomposition temperature of plain PLA is 360ºC. The plasticized PLAs were stable within the range of interest (10ºC). A shift from 360ºC to370ºC was observed for the decomposition temperature for PLA/PEG 15%. Different assumptions can be pointed out to explain the catalytic effect played by PEG to degrade PLA. The products of PEG degradation generated when the initial degradation temperature is reached can promote PLA degradation. The reaction between hydroxyl terminated groups of PEG and PLA ester functions, acidity, catalysts or some impurities could be the sources of such degradation. Blending of R.ACID in PLA matrix was entirely different from other plasticizers, R.ACID decreased the Td from 359 to 348.9°C.

3.4. Melt flow index and density

Melt flow index (MFI) is a measure of the ease of flow of the melt of a thermoplastic polymer. Knowing the MFI of a polymer is vital to anticipating and controlling its processing. In Table 3 MFI value of neat PLA was absorbed to be 3.8 g/10min, addition of PEG in PLA matrix shows MFI value of 29.8 g/10 min, 35.6 g/10 min and 50.7 g/10 min for 5, 10 and 15 wt% of PEG. R.ACID changes the MFI value of neat PLA from 3.8g/ 10 min to 10.6 g/10 min, 20.1 g/ 10 min and 29.3 g/10 min for 5, 10 and 15 wt%. Effect of PBS on MFI is found to lower than that of other plasticizers, starting from 9.2 g/10min to 29.3 g/10 min. MFI values of all the plasticizers revealed that PEG decreased the viscosity of PLA blend very effectively by increasing the MFI than other PLA plasticized blend.

Table 3. MFI and Density of neat PLA and plasticized PLA

Material	MFI (G/10 Min)	Density (G/Cc)
PLA 100%	3.8	1.1
PLA90%PBS10%	9.2	1.1
PLA80%+PBS20%	10.6	1.2
PLA70%+PBS30%	13.7	1.2

PLA95%+PEG5%	29.8	1.2
PLA90%+PEG10%	35.6	1.2
PLA85%+PEG15%	50.7	1.2
PLA95%+R.ACID5%	10.6	1.2
PLA90%+R.ACID10%	20.1	1.2
PLA85%+R.ACID15%	29.3	1.2

3.5. SEM analysis

Since the mechanical properties of multiphase polymer blends depend largely on the phase morphologies, SEM was employed to identify the phase structure of the binary blends. Figure 1. (a) to Figure 1.(i) shows surface SEM micrographs of various PLA-based blends. As observed from Figure 1. (a) the round particles indicates the PBS phases every distributed within the PLA matrix. As shown in Figure 1. (a), the PBS particles were well dispersed in PLA matrix for the blend containing 10 wt% PBS. With increasing content of PBS, the amount of the big PBS particles increased. In PLA matrix it can be seen that the interface between PBA and PLA phases was not distinct. This indicated that a relatively strong interaction between PBA and PLA matrix existed. In all the SEM images (Figure 1. (a) to Figure 1. (c)) of PLA/PBS was found to be uniformly distributed within the PLA matrix.

From Figure1.(d) to Figure1. (f) Dispersion of PEG in the PLA matrix was clearly visible, in which PEG particles dispersed uniformly. So it could be inferred that interaction between PLA and PEG was effectively good. In the case of R.ACID, SEM image (Figure 1. (g) to Figure 1. (i)) found to be clean and clear except some contamination in the PLA matrix. In every formulations, flow marks and die marks were found to be increased in the sheet surface with increase in plasticizer content in the PLA matrix (i.e., because of increase in plasticizing effect of the plasticizer in PLA matrix).

4. Conclusion

In the present study various plasticised, PLA sheets were developed and characterized. PEG and R.ACID were found to be good plasticizer for PLA whereas PBS did not plasticizes PLA. Addition of plasticizers changes the glass transition temperature of PLA sheet. For PEG and R.ACID plasticized PLA sheet tensile strength decreased with increase in plasticizer content. The percentage elongation at break remains almost same as neat PLA and PBS plasticizes PLA but in the case of PEG and R.ACID increase in percentage of elongation upto 9.4% and 11.9% was observed. Increase in tear strength was observed. It was found that 25% of reduction in Tg by R.ACID. SEM image of all the blends shows uniform distribution of plasticizers in PLA matrix.

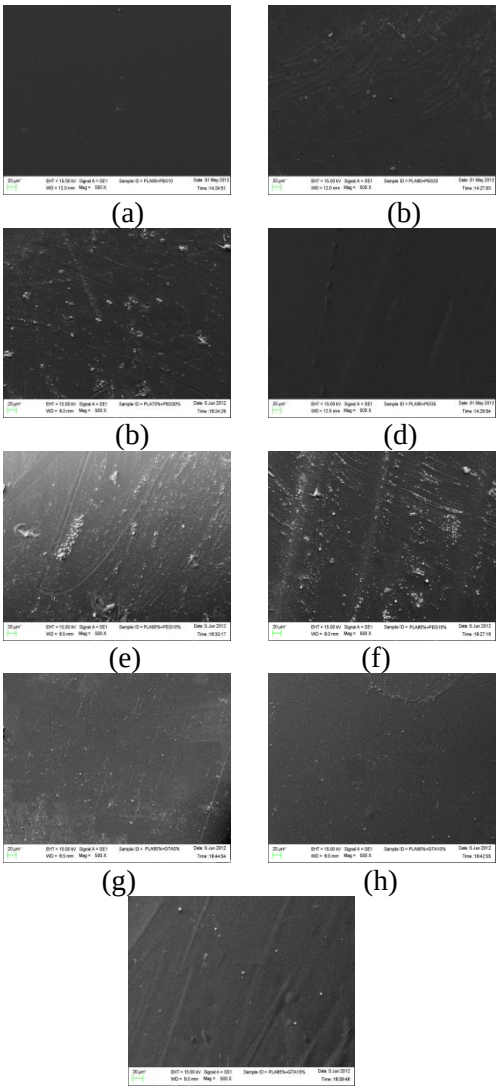

Figure 1. SEM images of (a) PLA/PBS 10%, (b) PLA/PBS 20%, (c) PLA/PBS 30%, (d) PLA/PEG 5%, (e) PLA/PEG 10%, (f) PLA/PEG 15%, (g) PLA/R.ACID 5%, (h) PLA/R.ACID 10%, (i) PLA/R.ACID 15%.

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